

**AMENDMENTS TO THE SPECIFICATION:**

***Page 6, replace the paragraph starting at line 5 with the following paragraph:***

Physical method is to apply a pulsed plating (PP) or periodic pulse reverse (PPR) with both positive and negative pulses (etc., a waveform to the cathode / anode system). Periodic pulsed plating (PPR) techniques could reduce the formation of voids because the rate of metal deposition inside a trench is nearly the same as the rate at the upper portion. It is virtually like a deposition / etching sequence. It can produce a deposition / etching sequence that polish copper in the high-density regions more quickly than in the low-density regions, and produce the required gap fill capability. Pulsed plating (PR) can decrease the effective mass transfer boundary layer thickness and thus produce higher ~~instaneous~~ instantaneous plating current density as well as better copper distribution. Decreasing thickness of boundary layer could lead to significant concentration overpotentials decreased. Therefore, the filling capability could be enhanced in a high aspect ratio of via / trench.

***Page 6, replace the paragraph starting at line 19 and bridging pages 6 and 7 with the following paragraph:***

Chemical method is to add organic additives in the electroplating solution. A widely used electroplating solution consists of many additive ~~groups~~ groups (e.g. thiourea, ~~aeetylthiourea~~ acetylthiourea, naphthalene sulfonic acid). However, levelers are chemicals with an amine group (e.g. tribenzylamine). Carrying ~~agent~~ agents could promote the deposition of ductile copper, while brightener and leveling ~~agent~~ agents level out non-uniform substrates during electrodeposition. In order to make ~~electrodeposition~~ electrodeposition on a small dimension very well (in very high aspect ratios for future ULSI metallization), an understanding of additive agent is required to further study. Establishing

proper agents in a specific action and a proper concentration ratio often determines the success of a gap filling plating process.

***Page 8, replace the paragraph starting at line 9 and bridging pages 8 and 9 with the following paragraph:***

In 1998, CuTek Research Inc. developed a new deposition system, which has a standard cluster tool configuration with a fully automatic dry/clean wafer in and dry/clean wafer out operation. Cu electroplating is performed on a Cu seed layer with a thickness of 30-150nm. A sputtered Ta or TaN with 30nm thickness is used as a barrier and an adhesion layer, respectively. An excellent gap filling with thicker deposited in the trenches than on top of the field surface could be achieved using pulse plating (PP) and periodic pulse ~~reverses~~ reverses (PPR) with suitable additive agents. Dual damascene structures with 0.4  $\mu\text{m}$  feature size in an aspect-ratio of 5:1 and deep contact structures with 0.25  $\mu\text{m}$  feature size in an aspect-ratio of 8:1 could be completely filled without any void or seam function. The impurity contained in electroplated Cu film is measured to be below 50ppm. The major contaminants found were H, S, Cl, and C. A higher concentration of these elements is measured at the edge of wafer in comparison with the center. This is probably due to high hydrogen evolution and higher organic additive incorporated at the high current density region.

***Page 11, replace the paragraph starting at line 7 and bridging pages 11 and 12 with the following paragraph:***

P-type (001) oriented single crystal silicon wafers of 15-25  $\Omega\text{-cm}$  in 6-inch diameter were used as deposition substrates in this work. The blank wafers were first cleaned by a conventional wet cleaning process. After wet cleaning, wafers were treated with a dilute 1:50

HF solution before loading into a deposition chamber. A 50-nm-thickness of TiN and a 50-nm-thickness of Cu were deposited using conventional ~~PVD~~ PVD to act as a diffusion barrier and a seed layer, respectively. Patterned wafers were fabricated to examine the ability of Cu electroplating in small trenches and vias. After standard RCA cleaning, wafers were treated with thermal oxidation. Then, a photolithography technique with reactive ion etching (RIE) was used to define a definite dimension of trenches/vias. A 40-nm-thickness of TaN used as barrier and a 150-nm-thickness of Cu used as a seed layer were deposited by ionized metal plasma (IMP) PVD, respectively. The dimension of trench/via was defined between 0.3-0.8  $\mu\text{m}$ . An electroplating solution, which was used for Cu electroplating, was usually composed of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{H}_2\text{SO}_4$ , Cl, additives, and wetting agent. The compositions of the electroplating solution were described in Table 2. Additives were frequently added in Cu electroplating because they worked as brightening, hardening, grain refining, and leveling agents. The current density applied was 0.1-4  $\text{A}/\text{dm}^2$ . Besides, Cu(P) (Cu: 99.95 %, P: 0.05 %) material was used as an anode to supply sufficient Cu ions and made good quality of Cu electroplated films.

***Page 15, replace the paragraph starting at line 15 and bridging pages 15–18 with the following paragraph:***

In experiment, we keep concentrations of sulfate acid ( = 197g/l) and sulfate copper (90g/l) constant. Since conductivity of solutions is higher, and anode and cathode polarization are small, voltage required for Cu deposition is small. Change in sulfate acid concentration has more influence than changes in copper sulfate concentration in solution conductivity and anode and cathode polarization. Fig. 9 shows the relation between applied current change and Cu deposition rates. It is found that deposition rate increases with increasing applied current. The deposition rate reaches a maximum when applied current

increase increases to  $3.2 \text{ A/dm}^2$ . As shown in Fig 10, we can see the resistivity changes with different applied current. When applied current is at  $3.2 \text{ A/dm}^2$ , the resistivity ~~become~~ becomes very large. Figs.11(a) and 11(b) present film morphology of Cu electroplated on seed layer / TiN / Si at various current densities ( $1\text{-}4 \text{ A/dm}^2$ ) without additive addition. Large grain of Cu film is observed at high current density. The resistivity exhibits unusually high ( $\sim 10 \mu\text{m-cm}$ ) when high current is applied. A high resistivity of Cu film observed could be ~~attribute~~ attributed to rough surface formation, which resulted in film non-conformity at high current condition. The rough surface formed at high current could be rationalized by following postulations. It was supposed that Cu electroplating rate depended on Cu ions diffusion onto a substrate surface. At high current applied, most of Cu ions were effected at a high electric field; therefore, Cu ions diffusion from solution to substrate surface was very fast. Since Cu ion diffusions was very fast, the depletion of Cu ions in diffusion layer was very rapid; Cu ions could ~~be~~ not be supplied instantly from electroplated solution into a diffusion layer. The Cu electroplating was limited by Cu ion diffusion. This was called diffusion controlled. Since no replenish of Cu ions diffused onto substrate ~~surface~~ surface, no more of nucleation was formed on the surface. Cu aggregation could occur on the surface due to high electric field effect. A rough surface formed was ascribed to Cu agglomeration. Fig. 12 ~~present~~ presents relative intensity ratio of Cu(111)/Cu(002) by X-ray diffraction measurement at various applied current density. According to XRD results, a strong (111) orientation was always observed at higher current density applied. The development of growth orientation of the copper film could be rationalized by considering surface energy and strain energy at different crystal ~~orientation~~ orientations. In the initial stage, the orientation of Cu (002) plane was formed because this plane possessed the lowest surface energy. As applied electrical current was increased, the strain energy becomes a dominant factor in

governing grain growth. The peak intensity of Cu (111) was increasing at high electrical current applied because of high strain energy in Cu (111) orientation. In addition, a Cu (111) orientation was preferred because this orientation showed better electromigration resistance. Contradictory, Cu (111) formed at high current density could make a surface more roughness rougher as shown in Fig. 16 (b). In order to improve the filling of Cu electroplating, it was attempted to add some additives in electroplating solution. A high resistivity of Cu film at high current was also analyzed by SIMS and compared with that at low current condition (see ~~Fig.~~ Figs. 13 a & b). The oxygen concentration in the high resistivity of Cu film is higher because of its rough surface with film non-conformity at high current condition.

***Page 18, replace the paragraph starting at line 17 and bridging pages 18–20 with the following paragraph:***

Various organic and inorganic additives are added in solution to help Cu electroplating. Thiourea is a common additive, which usually added in electroplating solution. As presented in Fig. 18, the resistivity of electroplated Cu films does not show big difference when the concentration of ~~Thiourea~~ thiourea is smaller than 0.054 g/l. A high resistivity is observed when ~~Thiourea~~ thiourea is more than 0.054 g/l. Fig. 19 presents the SEM image of Cu (111) at 0.03 g/l of ~~Thiourea~~ thiourea addition. The current is applied at 2.4 A/dm<sup>2</sup>. As shown from SEM image, addition of additives could help (111) formation at low current density, because the additive could be incorporated into the deposit to provide a specific growth orientation. Fig. 20 presents the SEM image of the electroplated Cu film at 0.054 g/l of ~~Thiourea~~ thiourea addition. The current applied is still to keep at 2.4 A/dm<sup>2</sup>. As shown in Fig 20, when concentration of ~~Thiourea~~ thiourea is increasing, the dendrite produced during Cu electroplating is increasing. This dendrite has similar geometric structure with diffusion-limited clusters. Moreover, ~~Thiourea~~ thiourea could decompose to

form pernicious product ( $\text{NH}_4\text{SCN}$ ) which results in embattlement of electroplated Cu films. Fig. 21 shows the resistivity of copper film change with deposition time. It is appeared that resistivity is lower when the copper film become large block. Because that the grain boundary of copper film is decreasing to make surface more smooth than initial thin film. The resistivity of Cu film is higher when ~~Thiourea~~ thiourea is added. According to SIMS results [Fig. 22(a)(b)(c)], we can find the concentration of S element is increased with increasing concentration of ~~Thiourea~~ thiourea. It is suggested that ~~Thiourea~~ thiourea adsorbed on the surface of the cathode could make the resistivity of Cu increasing. In addition, voids is are formed when ~~Thiourea~~ thiourea is used as additive agent.

*Page 20, replace the paragraph starting at line 6 and bridging pages 20–21 with the following paragraph:*

PEG (polyethylene glycol) is widely used in Cu electroplating as a carrier agent. In this study, we use different molecular weight of PEG (200~10,000) and added in electrolyte with HCl and small amount of ~~Thiourea~~ thiourea (0.0036g/l), since small amount ~~Thiourea~~ thiourea could help (111) plan formation. We can ~~found~~ determine the larger molecular weight (m.w.>200) make the higher resistivity of copper film. According to Fig. 23, the resistivity of copper film is increasing with PEG molecular weight higher with deposition time. It is suggested that the longer chain ~~length with Thiourea~~ length with thiourea is absorbed on the surface of the substrate. From SEM image shown in Fig. 24(a)(b), film morphology doesn't change a lot when PEG molecular weight is increasing, but the plane (111) is decreasing when PEG molecular weight is increasing. [Fig. 25] According to SIMS analysis [shown in Fig. 26(a)(b)], the major components of Cu film are still Cu, O, C, S and Ti. The amount of S element will be increasing with increasing molecular weight of PEG. This observation is proved by our suggestion which discussed previously.

*Page 21, replace the paragraph starting at line 2 with the following paragraph:*

Based on our results, a lot of ~~Thiourea~~ thiourea and larger molecular weight of PEG (m.w >200) could not be used as additives in Cu electroplating for future Cu interconnect because of higher resistivity of copper film and poor cap-filling ability. In order to make Cu electroplating implemented in ULSI processing, a suitable additive must be developed. In this study, we try new traditional additive agents of ~~Molasses~~ molasses which shows the same effect on resistivity of copper film.

*Page 21, replace the paragraph starting at line 9 with the following paragraph:*

Glucose is also a common traditional additive agent used in Cu electroplating. In our experiment, we found the resistivity and orientation of electroplated copper film do not ~~obvious~~ obviously change with different amount of ~~Glucose~~ glucose. However, filling capability in via and trench is poor. Although an equal thickness at all points of a feature is formed, a void still appears in the trench.

*Page 24, replace the paragraph starting at line 2 with the following paragraph:*

~~Another~~ Other organic additives with unsaturated  $\pi$ -~~bands~~ bonds, like ~~Tribenzylamine~~ tribenzylamine, benzotriazole and naphthalene sulfonic acid, could be considered to be ~~use~~ used as additives in Cu electroplating. Since they have unsaturated  $\pi$ -~~bands~~ bonds, the  $\pi$  electrons could interact with surface atoms of copper, to produce substantial effect on the properties of deposits. Brightness, leveling, as well as stability effect is still needed to do further study. This study, we try to use ~~Tribenzylamine~~ tribenzylamine and benzotriazole as leveling agents. However, these levels agents are quite difficult in soluble in sulfate acid solution to make experiment unworkable.

*Page 27, replace the paragraph starting at line 19, bridging pages 27 and 28 with the following paragraph:*

Fig. 6. Dependence of the thickness vs.  $\text{H}_2\text{SO}_4$  concentration change.  
( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  at 90 g/l, current density at  $2.4 \text{ A/dm}^2$   ~~$\text{A/dm}^2$~~  and time at 2 min)

*Page 28, replace the paragraph starting at line 3 with the following paragraph:*

Fig 7. Cu films resistivity change as a function of concentration of  $\text{H}_2\text{SO}_4$   
( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  at 90 g/l,  $\text{H}_2\text{SO}_4$  at 90 g/l, current density at  $2.4 \text{ A/dm}^2$   ~~$\text{A/dm}^2$~~   
at 2 min).

*Page 28, replace the paragraph starting at line 6 with the following paragraph:*

~~Fig 8~~ Figs. 8a and 8b SEM images of copper film morphology with an without  $\text{H}_2\text{SO}_4$   
presence. (a) only  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (90 g/l) (b)  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (90 g/l)  
&  ~~$\text{H}_2\text{SO}_4$~~   $\text{H}_2\text{SO}_4$  (20 ml/l)

*Page 28, replace the paragraph starting at line 9 with the following paragraph:*

Fig. 9. Dependence of film deposition rate vs. current density variation.  
( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  at 90 g/l,  ~~$\text{H}_2\text{SO}_4$~~   $\text{H}_2\text{SO}_4$  at 197 g/l and time at 2 min)

*Page 28, replace the paragraph starting at line 11 with the following paragraph:*

Fig. 10. Film resistivity change as a function of applied current variation.  
( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  at 90 g/l,  ~~$\text{H}_2\text{SO}_4$~~   $\text{H}_2\text{SO}_4$  at 197 g/l and time at 2 min)

*Page 28, replace the paragraph starting at line 13 with the following paragraph:*

~~Fig 11~~ Figs. 11a and 11b Cu film morphology at different applied ~~current~~ currents.



*Page 28, replace the paragraph starting at line 14 with the following paragraph:*

Fig. 12. XRD measurement at various applied ~~current~~ currents.

(CuSO<sub>4</sub>·5H<sub>2</sub>O at 90 g/l, H<sub>2</sub>SO<sub>4</sub> ~~H<sub>2</sub>SO<sub>4</sub>~~ at 197 g/l and time at 2 min)

*Page 28, replace the paragraph starting at line 16 with the following paragraph:*

Fig. 13.(a) The SIMS results showed that oxygen ~~eoneentraten~~ concentration in electroplated Cu film at low applied current density of 1.2A/dm<sup>2</sup> ~~A/dm<sup>2</sup>~~.

*Page 28, replace the paragraph starting at line 18 with the following paragraph:*

Fig. 13.(b) The SIMS results showed that oxygen ~~eoneentraten~~ concentration in electroplated Cu film at high applied current density of 3.2A/dm<sup>2</sup> ~~A/dm<sup>2</sup>~~.

*Page 28, replace the paragraph starting at line 22 with the following paragraph:*

Fig 15 The relationship of Cu film resistivity vs. various concentration of HCl (CuSO<sub>4</sub>·5H<sub>2</sub>O at 90 g/l, H<sub>2</sub>SO<sub>4</sub> at 197 g/l, current density at 2.4 A/dm<sup>2</sup> ~~A/dm<sup>2</sup>~~ at 2 min).

*Page 28, replace the paragraph starting at line 24 with the following paragraph:*

Fig 16: Figs 16a and 16b The uniformity at the top of the trench is (a) not smooth without HCl addition (b) more smooth with HCl addition.

*Page 28, replace the paragraph starting at line 27 with the following paragraph:*

Fig 18 The relationship of Cu film resistivity vs. various concentration of (NH)<sub>2</sub>CS. (CuSO<sub>4</sub>·C<sub>5</sub>H<sub>2</sub>O at 90 g/l, H<sub>2</sub>SO<sub>4</sub> at 197 g/l, HCl at 70 ppm, current density at 2.4 A/dm<sup>2</sup> ~~A/dm<sup>2</sup>~~ at 2 min).

***Page 28, replace the paragraph starting at line 30 with the following paragraph:***

Fig 19 SEM image of the electroplated Cu film at 0.03 g/l of thiourea addition, applied current density is 2.4 ~~A/dm<sup>2</sup>~~ A/dm<sup>2</sup>.

***Page 28, replace the paragraph starting at line 32 with the following paragraph:***

Fig 20 SEM image of the electroplated Cu film at 0.054 g/l of thiourea addition, applied current density was 2.4 ~~A/dm<sup>2</sup>~~ A/dm<sup>2</sup>.

***Page 28, replace the paragraph starting at line 34 with the following paragraph:***

Fig 21 The relationship of Cu film resistivity vs. deposition time ((CuSO<sub>4</sub>C<sub>5</sub>H<sub>2</sub>O at 90 g/l, H<sub>2</sub>SO<sub>4</sub> at 197 g/l, HCl at 70 ppm current density at 1.2 ~~A/dm<sup>2</sup>~~ A/dm<sup>2</sup>).

***Page 29, replace the paragraph starting at line 2 with the following paragraph:***

Fig 23 The resistivity of Cu films change with various PEG molecular weight at different deposition time. (CuSO<sub>4</sub>·5H<sub>2</sub>O at 90 g/l, H<sub>2</sub>SO<sub>4</sub> ~~H<sub>2</sub>SO<sub>4</sub>~~ at 197 g/l, HCl at 70 ppm, current density at 1.2 ~~A/dm<sup>2</sup>~~ A/dm<sup>2</sup>).

***Page 29, replace the paragraph starting at line 5 with the following paragraph:***

Fig 24 Film morphology analysis with different amount of ~~Thiourea~~ thiourea.

***Page 29, replace the paragraph starting at line 7 with the following paragraph:***

Fig. 25 XRD measurement at various PEG molecular ~~weight.~~ weight.

***Page 29, replace the paragraph starting at line 8 with the following paragraph:***

Fig. 26(a) The SIMS analysis on Cu film with ~~Thiourea~~ thiourea and PEG200 addition.

*Page 29, replace the paragraph starting at line 10 with the following paragraph:*

Fig. 26(b)      The SIMS analysis on Cu film with ~~Thiourea~~ thiourea and PEG4000 addition.